Direct observation of the intersystem crossing in poly(3-octylthiophene)

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Using subpicosecond photoinduced absorption, we monitor the evolution of singlet excitons in solutions of regiorandom poly(3-octylthiophene) (P3OT), regioregular poly(3-hexylthiophene) (P3HT), and a well-defined α-oligothiophene with 12 repeat units (T_{12}). We find a luminescence lifetime of 500 ps, and we observe the intersystem crossing from the singlet manifold to the triplet manifold, with a rate constant of $k_{\mathrm{ISC}}^{-1}=1.2$ ns. By measuring the quantum efficiency of luminescence, we estimate an intrinsic lifetime of 2 ns for the singlet excitons, and a nonradiative decay rate of $k_{\mathrm{nr}}^{-1}=1.5$ ns. We find no difference in the intersystem crossing time for the different thiophene derivatives, implying the intersystem crossing rate is determined primarily by the relatively large spin–orbit interaction due to the sulfur heteroatom and not by chain defects, chain ends, or effects due to the side groups. In addition, we find that for $t<50$ ps a fraction of the photoexcitations undergo one-dimensional diffusion limited recombination. © *1995 American Institute of Physics.*

INTRODUCTION

Triplet excited states play an important role in the photophysics of conjugated polymers and in the photophysics of many biological systems. In derivatives of finite polyenes, triplet states control electronic relaxation pathways in the processes of vision[1] and photosynthesis.[2] With the advent of polymer light-emitting diodes (LED's), the interest in understanding the dynamics of the triplet state has increased[3] since the intersystem crossing from the singlet to the triplet manifold provides an additional relaxation pathway that competes with luminescence, thereby affecting the efficiency of the LED.

To the best of our knowledge, the intersystem crossing rate from the singlet manifold to the triplet manifold has not been accurately determined in any conjugated polymer. Indirect evidence exists for a subpicosecond intersystem crossing time in poly(p-phenylene–vinylene),[4,5] but the absence of significant luminescence quenching suggests an intersystem crossing time of 500 ps or more, as is typical of small organic molecules.[6] We have used subpicosecond photoinduced absorption (PIA) spectroscopy to study the photophysics of poly(3-octylthiophene) (P3OT), poly(3-hexylthiophene) (P3HT), and a twelve unit oligothiophene (T_{12}), in solution. We have identified the PIA features arising from the $S_1 \rightarrow S_n$ transition of the singlet exciton and the $T_1 \rightarrow T_n$ transition of the triplet exciton. The PIA peaks of the two species are spectrally resolved, allowing us to unambiguously detect the onset of the $T_1 \rightarrow T_n$ absorption. By fitting to the PIA decay kinetics at the peak of the $T_1 \rightarrow T_n$ absorption, we obtain the intersystem crossing time. This experiment provides the first direct measurement of the intersystem crossing time in a conjugated polymer.

EXPERIMENT

The pulsed laser instrumentation used for fast transient PIA measurements consisted of an amplified CPM laser system producing 100 fs pulses at 2.01 eV with typical pulse energies of 4 μJ; details have been described in a previous publication.[7] For this work, the 4 μJ, 2 eV pulse from the amplified CPM laser was used to generate a continuum ''white light'' pulse in a 3 mm flowing ethylene glycol cell. Approximately 4% of the continuum pulse was split off using the front face of a beam splitter and was used to probe the absorption of the sample. The remaining light was passed through a broadband (2.3–2.6 eV) bandpass filter and used as the pump beam to photoexcite the sample.

The pulse width of the 2.4 eV pump pulse was measured using second-harmonic generation in a BBO crystal and found to be 250 fs. We also measured the pulse width of the continuum probe pulse using two-photon absorption in ZnSe,[8] which yielded a probe pulse width at 1.48 ± 0.05 eV of 500 fs and of 550 fs at 1.21 ± 0.05 eV.

The millisecond time scale PIA experiments and the measurement of the steady-state luminescence spectrum used steady state techniques as described previously.[9] To measure the time resolved luminescence, we used a Hamamatsu streak camera and photoexcited the sample at 2.5 eV using a frequency doubled mode-locked Ti:Sapphire laser. The time resolution of this experiment was determined to be 50 ps. A 10 nm bandpass filter was inserted in front of the streak camera to select the spectral region to be measured.

Samples were prepared in a 2 mm thick solution cell containing a 7×10^{-4} M solution of chromophore in xylene. Three related systems were studied: regiorandom poly(3-octylthiophene), P3OT, regioregular poly(3-hexylthiophene), P3HT, and a well-defined α-oligothiophene, T_{12}, containing 12 thiophene units.[10] Since these concentrations are below the overlap concentration,[11] we consider the polymer and oligomer chains to be isolated from one another in solution. The P3HT contained greater than 99% regioregular head-to-tail structure,[12] reducing its solubility compared to the regiorandom P3OT. At the concentrations employed, however, the absorption spectrum indicated that the P3HT was well dissolved. To ensure a low concentration of oxygen in the solutions, the samples were put through approximately ten

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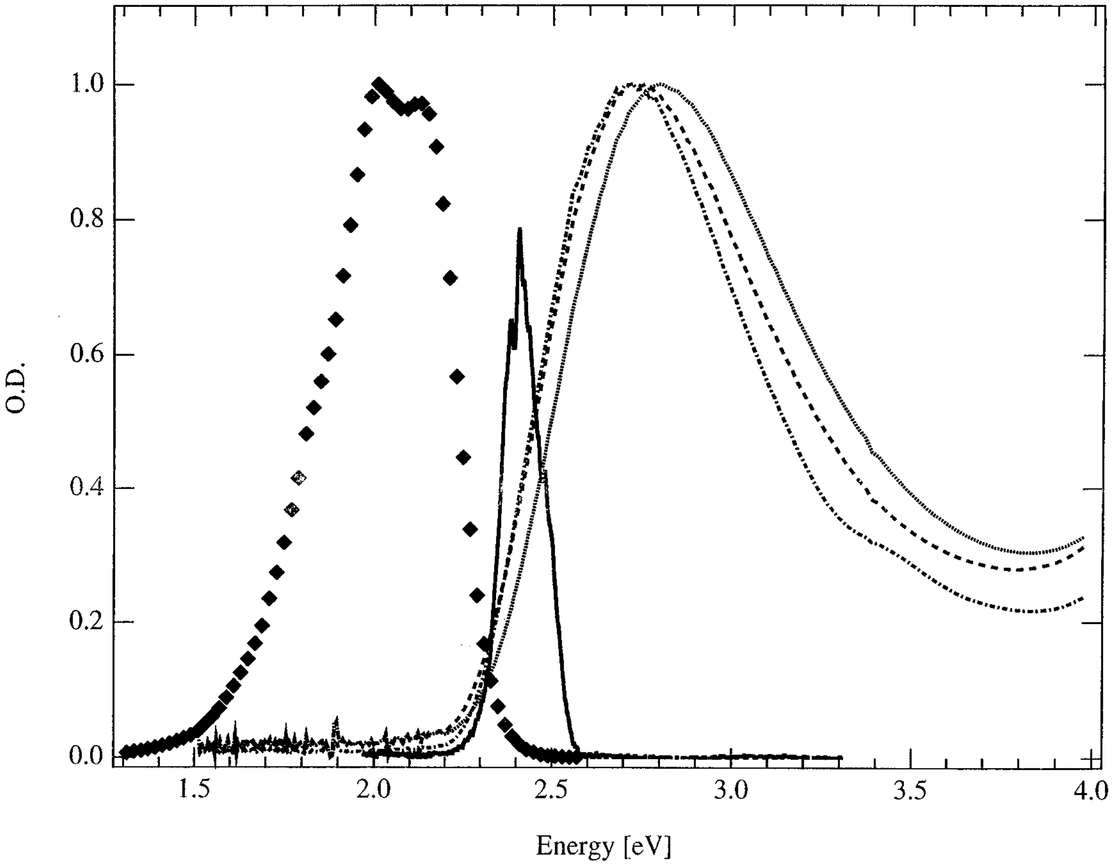

FIG. 1. The dotted line shows the normalized linear absorption of a 7×10^{-4} M solution of P3OT in xylene at room temperature. The dashed line is for the same concentration solution of P3HT in xylene, and the dotted-dashed line is for the same concentration solution of T_{12} in xylene. The solid diamonds show the photoluminescence spectrum of the same solution of P3OT, pumped using the 488 nm line of an Ar^+ laser. The solid line is the spectrum of the 250 fs pump pulse used to photoexcite the sample.

freeze–pump–thaw cycles prior to conducting any experiment. All experiments were conducted at 300 K, and fresh samples were used for all the experiments since it has been observed that polythiophene derivatives in solution degrade upon exposure to light over a period of several days.[11]

RESULTS AND DISCUSSION

The linear absorption spectra of P3OT, P3HT, and T_{12} in solution are shown in Fig. 1. In solution, the onset of the $\pi-\pi^*$ transition is blue shifted by approximately 300 meV compared to P3OT as a solid film, indicating that the average conjugation length in solution is less than in the solid phase. Indeed, the band gap of T_{12} is slightly less than P3OT in solution, implying the average conjugation length of P3OT in solution is on the order of 10 monomer units. This agrees with the results of small-angle neutron scattering done on a slightly different polythiophene derivative, poly(3-butylthiophene), in solution[13] which indicated a statistical length of 13 monomer units, and with light-scattering studies which found a persistence length of 2.4 nm for P3HT in dilute solution in THF.[11] The conjugation length of regio-regular P3HT in solution is most likely slightly longer than the regio-random P3OT, since ordering of the side chains leads to an increased stiffness of the polymer backbone.[14] This is supported by the slightly smaller band gap observed for the regio-regular polymer in solution than for P3OT. Studies on poly(3-hexylthiophene) and thiophene oligomers with five repeat units in solution have been analyzed in terms of polarons and bipolarons as the charged photoexcitations.[15,16] Hence we consider that the concept of electron-hole confinement via a shared lattice distortion to be applicable for the samples used in this study.

The spectrum of the 250 fs pump pulse used to photoexcite the polymer also is shown in Fig. 1. We pump directly into the $\pi-\pi^*$ absorption band so that the initial photoexcitation is of B_u symmetry, and we avoid any ambiguities associated with pumping into higher excited states. In addition, the room-temperature luminescence obtained by pumping with the 488 nm line of the Ar^+ laser is shown in Fig. 1. Since the spectrum of the luminescence extends down to 1.5 eV, care was taken to not probe the sample at energies greater than 1.5 eV to avoid depopulating the singlet states through stimulated emission.[17]

The time-resolved PIA of P3OT in solution is shown in Fig. 2. Note that the time axis increases coming out of the page. At 2 ps, the earliest time shown in Fig. 2, a strong PIA feature is apparent, peaking near 1.22 eV. This feature was found to be linear in pump intensity. The PIA spectrum from

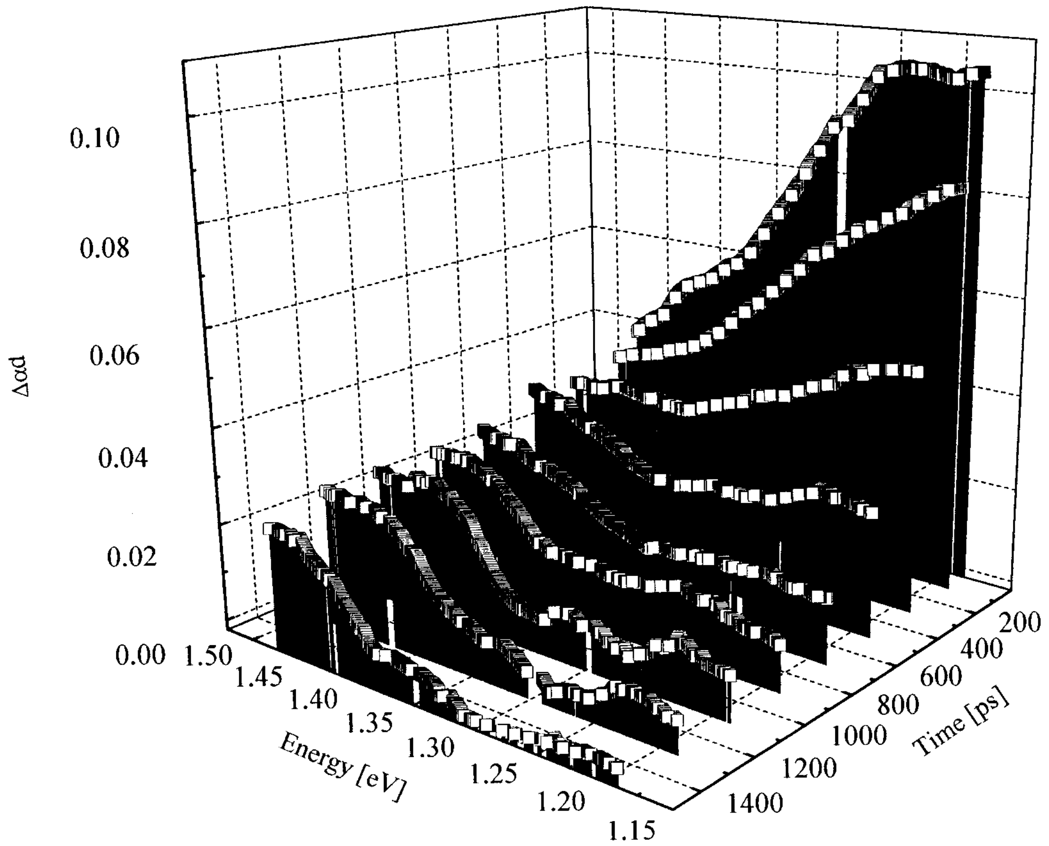

FIG. 2. The photoinduced absorption spectrum of P3OT in xylene after being pumped by a 250 fs, 2.4 eV pump pulse. Note that the time axis increases coming out of the page.

1.5 to 2.0 eV is not available since it is dominated by the strong gain which results from stimulated emission of the luminescent singlet exciton. By 500 ps the spectrum has changed with a new feature emerging at 1.5 eV. This feature is longer lived than the 1.22 eV feature and by 1.5 ns dominates the PIA spectrum.

Since the lifetime of the fluorescence is 500 ps (the fluorescence kinetics will be discussed more later), the problem of gain through stimulated emission does not affect the PIA spectrum at 1.5 ns. Hence, we are able to extend the PIA spectrum at 1.5 ns from 1.2 to 2.0 eV. Figure 3 shows that the PIA spectrum at 1.5 ns matches that seen in the same sample in the ms regime. The dependence of the PIA signal on the pump fluence is linear at both 1.5 ns and in the ms regime, implying the photoexcitation decays monomolecularly. This is confirmed through fitting the chopping-frequency dependence of the PIA in the ms regime; the data are best fit using a monomolecular decay function[18] (see inset in Fig. 3). The fit yields a lifetime of 77 μs for this excitation.

The absence of strong oscillations in the photoexcitation spectrum near the band edge (Fig. 3) implies that the 1.5 eV peak results from neutral excitations. Strong local electric fields develop in the presence of charged photoexcitations, leading to characteristic electroabsorption oscillations near the band edge.[19,20] This effect has been demonstrated in solutions of oligothiophene/C_{60}.[21] In this system photoinduced charge transfer occurs from the oligothiophene to C_{60}, resulting in the creation of charged excitations on the oligothiophene. The PIA of oligothiophene/C_{60} solutions shows strong oscillations near the band edge which closely follow the first derivative of the linear absorption band. The absence of similar features in the PIA spectrum observed for P3OT implies that the long-lived photoexcitations (with peak absorption in their excitation spectrum at 1.5 eV) are not charged.

The long lifetime, monomolecular decay, and neutral character of this excitation lead us to ascribe the 1.5 eV PIA feature in P3OT to a triplet–triplet transition. This conclusion is supported by the fact that the excitation is quenched by the presence of molecular oxygen in the solution, as shown in Fig. 3. In addition, recent work found a similar PIA feature in poly(3-alkylthiophene) (Ref. 22) which was also attributed to a triplet excitation.

In order to identify the origin of the PIA feature at 1.22 eV, we compare the decay kinetics of the 1.22 eV PIA to those of the luminescence, measured at the peak of the emission spectrum (1.96 eV); this comparison is shown in Fig. 4. Since the luminescence intensity is proportional to dn_s/dt (Ref. 23) (where n_s is the number density of singlet excitons), and the PIA is proportional to n_s, we would expect the derivative of the PIA at 1.22 eV to follow the kinetics of the luminescence, if this PIA feature comes from a singlet–singlet transition. Hence, if the population of singlet excitons

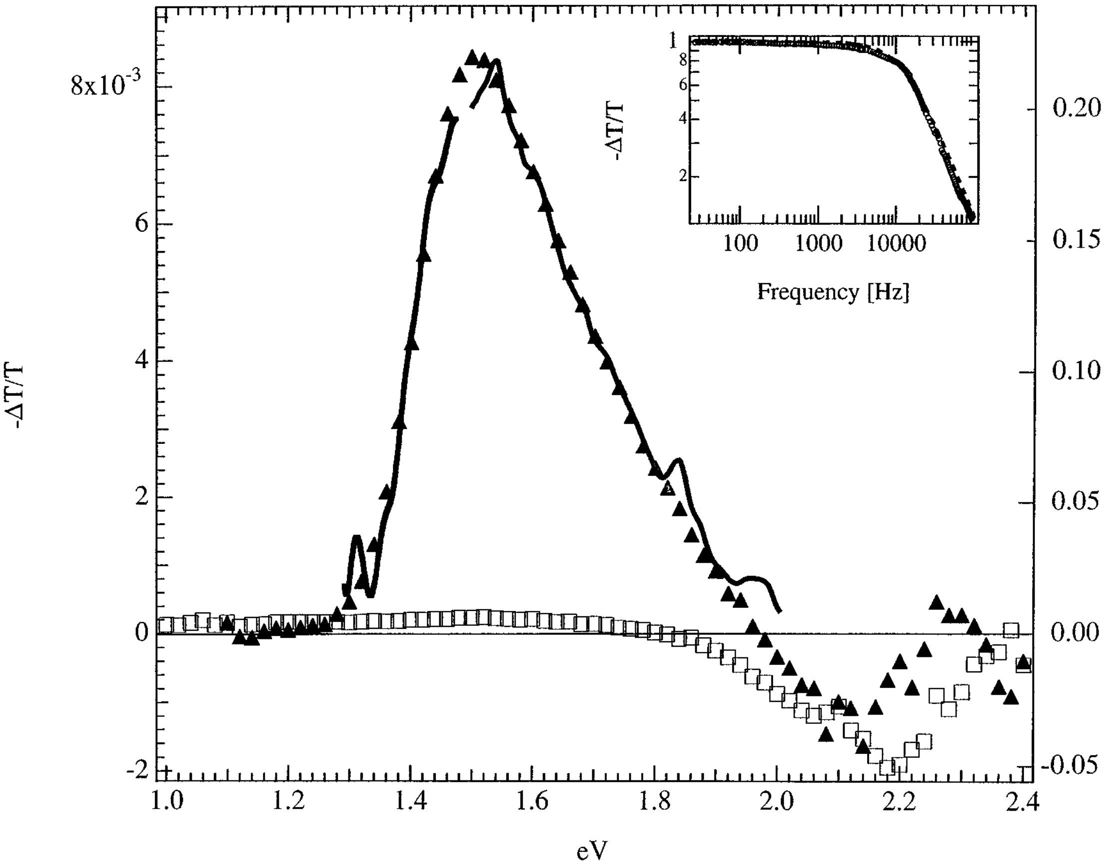

FIG. 3. The ms photoinduced absorption spectrum (solid triangles) of P3OT in xylene pumped by the 488 nm line of an Ar^+ laser. The solid line represents the photoinduced absorption of the same solution 1.5 ns after pumping the sample with a 250 fs, 2.4 eV pump pulse. The open squares show the ms PIA of the same solution prior to degassing the solution to remove oxygen. The inset shows the ms photoinduced absorption at 1.5 eV as a function of the chopping frequency fitted to a monomolecular rate equation.

decays exponentially, then the PIA and the luminescence should decay with the same lifetime. The data in Fig. 4, demonstrate that the two signals exhibit exponential decay kinetics with identical lifetimes; from the slope we obtain a lifetime of 500 ps. In addition, both signals exhibit a linear dependence on pump intensity, as expected for geminate recombination of singlet excitons. We, therefore, identify the 1.22 eV PIA feature as the $S_1 \rightarrow S_n$ transition of the singlet exciton. As the PIA features at 1.5 and 1.22 eV result from triplet–triplet and singlet–singlet transitions, respectively, the spectral shift shown as a function of time in Fig. 2 monitors the evolution of the photoexcitations from singlet excitons to triplet excitons.

In order to fit to the time decay of the PIA at 1.48 eV, we used the following rate equations:[24]

$$\frac{dn_S}{dt} = -kn_S, \tag{1a}$$

$$\frac{dn_T}{dt} = k_{\mathrm{ISC}} n_S - \beta n_T, \tag{1b}$$

$$k = k_{\mathrm{rad}} + k_{\mathrm{ISC}} + k_{\mathrm{nr}}. \tag{1c}$$

In Eq. (1), β is the rate constant for the $T_0 \rightarrow S_0$ transition ($\beta^{-1} = 77\ \mu\mathrm{s}$), k_{ISC} is the intersystem crossing rate, and k is the rate constant for the $S_1 \rightarrow S_0$ transition, and includes the rate constant for radiative recombination (k_{rad}), intersystem crossing (k_{ISC}), and all other nonradiative processes (k_{nr}). In writing Eq. (1) we have neglected all higher-order decay processes such as triplet–triplet or singlet–singlet annihilation. This is justified by the linear dependence of the PIA on pump fluence. In addition, since $\beta \ll k$, we can ignore the last term in Eq. 1(b) and thereby solve Eq. (1) analytically. The result is

$$n_T(t) = \frac{k_{\mathrm{ISC}}}{k} n_S(0)\{1 - e^{-kt}\}. \tag{2}$$

The PIA signal is given by the population of the given state times its molar extinction coefficient. The extinction coefficients for the $T_1 \rightarrow T_n$ and the $S_1 \rightarrow S_n$ transition are denoted by $\epsilon_T(\omega)$ and $\epsilon_S(\omega)$, respectively. The PIA signal at a given energy will be the sum of the contributions due to the $T_1 \rightarrow T_n$ transitions and the $S_1 \rightarrow S_n$ transitions. Hence, we used the following equation to fit to the decay kinetics of the PIA at 1.48 eV:

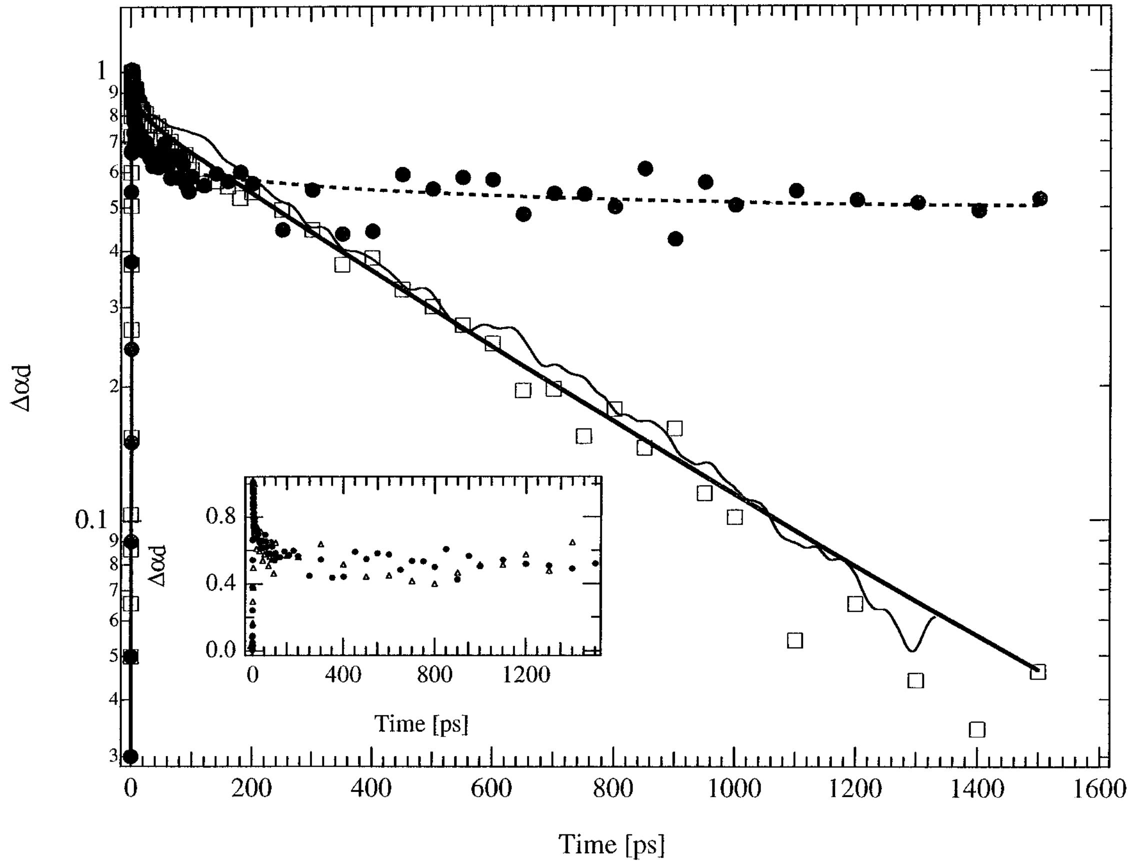

FIG. 4. Decay of the photoinduced absorption of P3OT at 1.5 eV (solid circles) and at 1.22 eV (open squares). The dashed line is the fit using Eq. (3), and the dotted line is a single exponential fit with a 500 ps time constant. The solid line is the luminescence decay at 1.96 eV. The inset shows the photoinduced absorption at 1.5 eV following excitation by a 2.4 eV pump pulse (solid circles) and a 4 eV pump pulse (open triangles).

$$\begin{aligned} &\Delta\alpha d(t,\omega)\\ &\quad\propto \epsilon_S(\omega)n_S(t)+\epsilon_T(\omega)n_T(t)\\ &\quad\propto \epsilon_S(\omega)n_S(0)e^{-kt}+\epsilon_T(\omega)\,\frac{k_{\mathrm{ISC}}}{k}\,n_S(0)\{1-e^{-kt}\}. \qquad (3)\end{aligned}$$

The extinction coefficient of each transition is related to the oscillator strength by[25]

$$f_{i\rightarrow f}=\frac{10^3\ \ln(10)m_e c^2}{\pi N e^2}\int \epsilon_{i\rightarrow f}(\omega)d\omega, \qquad (4)$$

where the subscripts i and f denote the initial and final state, N is Avagadro's number, m_e is the mass of the electron, and the other constants have their usual meaning.

An accurate determination of the ratio $\epsilon_T(\omega)/\epsilon_S(\omega)$ is unavailable, but since both transitions are dipole allowed, we assume that the ratio of the oscillator strengths, $f_{T_1\rightarrow T_n}/f_{S_1\rightarrow S_n}$ is of order unity. This allows us to set the relative magnitude of the extinction coefficients at the *peak* of their absorption spectra to be equal. From this we can estimate that the ratio of the extinction coefficients at 1.5 eV as $\epsilon_T(\omega=1.5\ \mathrm{eV})/\epsilon_S(\omega=1.5\ \mathrm{eV})\approx 1/2$. In order to get a more accurate determination of this ratio, knowledge of the wave functions involved is needed in order to calculate the dipole transition matrix elements. From Eq. (3), one sees that the result obtained for the intersystem crossing time is proportional to the ratio $\epsilon_T(\omega)/\epsilon_S(\omega)$ so that any fractional error resulting from the estimation of this quantity has a simple multiplicative effect on the result we obtain for the intersystem crossing time.

In order to fit the relaxation kinetics we used the following function:[26]

$$\Delta\alpha d(\tau)\propto\int dt I_{\mathrm{pb}}(t-\tau)\int dt' R(t-t')I_{\mathrm{pp}}(t'), \qquad (5)$$

with

$$R(t)=(1-e^{-t/\tau_1})(f(t)+Ae^{-(t/\tau_2)^{1/3}})\theta(t). \qquad (6)$$

In Eq. (5), $I_{\mathrm{pb}}(t)$ represents the probe pulse intensity profile, $I_{\mathrm{pp}}(t)$ represents the pump pulse intensity profile, and $R(t)$ is the response function which models the response of the system. The response function used is given in Eq. (6), where the first factor models the rise time, τ_1, of the system response and the second factor models the decay dynamics of the system. The function $f(t)$ is given by Eq. (3) and models the long term relaxation, while the second term in the brackets models the fast component ($t<50$ ps) of the decay. The function $\theta(t)$ is a unit step function.

Using Eq. (6) with $\epsilon_T(\omega)/\epsilon_S(\omega)=2$, we fit to the PIA dynamics of P3OT at 1.5 eV as shown in Fig. 4. The fit

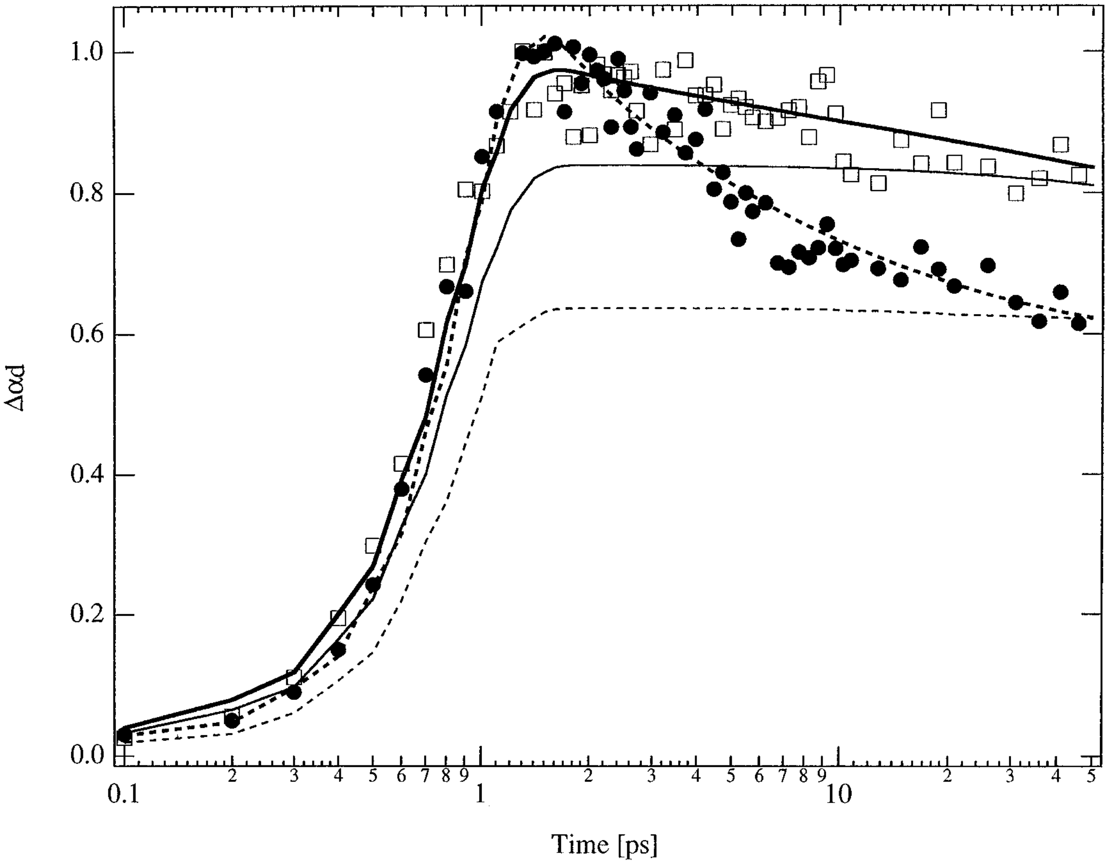

FIG. 5. The decay of the photoinduced absorption at 1.5 eV for $t<50$ ps for P3OT (solid circles) and T_{12} (open squares). The heavy dotted and heavy solid lines are fits using Eq. (5) with $A\neq 0$, and the thin dotted and thin solid lines show the fit when $A=0$.

yields an intersystem crossing time of 1.2±0.1 ns. Equation (3) alone provides an accurate fit for times greater than 50 ps. For $t<50$ ps, we must superimpose a stretched exponential onto the long term kinetics; we find the lifetime $\tau_2=1$ ps for P3OT, 2 ps for P3HT, and 4 ps for T_{12} (see Fig. 5). For comparison, Fig. 5 shows the fit without including the fast component ($A=0$). Finally, the rise time, τ_1, is found to be resolution limited (<500 fs) at both 1.5 and 1.22 eV.

The 1.2 ns result obtained for the intersystem crossing time is quite reasonable considering the spectra shown in Fig. 2, which gives us confidence that the estimate involved in fitting to the decay dynamics is appropriate. Within the error of the measurement, we obtained the same results for regioregular P3HT and for T_{12}. This indicates that the intersystem crossing time is insensitive to the defect level or to the configuration of the side chains. Hence, we conclude that the relatively large spin–orbit coupling constant of sulfur ($\xi=-184$ cm^{-1}) (Ref. 27) plays an important role in the intrinsic coupling of the singlet and the triplet manifolds.

In order to obtain an estimate of the rate constants k_{rad} and k_{nr}, we measured the luminescence spectra of a solution of P3OT in xylene and of the laser dye DCM in MeOH. The concentration of each solution was adjusted so the optical density at the laser pump wavelength of 488 nm was the same (OD≈0.75). Using the published value of 44% as the quantum efficiency of DCM in MeOH,[28] we obtain a quantum efficiency of 25% for P3OT in xylene. The intrinsic radiative lifetime is then calculated using

$$\tau_0=\tau/\mathrm{QE}, \tag{7}$$

where τ is the measured luminescence lifetime (=500 ps and QE is the quantum efficiency. This yields an intrinsic radiative lifetime of 2 ns for P3OT in xylene. The nonradiative lifetime can be calculated from Eq. (1c); we obtain 1.5 ns.

In addition, we compare the PIA at 1.5 eV after pumping at 2.4 and at 4 eV (see inset to Fig. 4). No difference is apparent in the decay of the two signals; we obtain the same intersystem crossing time using the 4 eV pump as given earlier for the 2.4 eV pump. In several molecular crystals it has been observed[29,30] that the intersystem crossing is more efficient from a higher excited singlet state. This was attributed to the larger energy difference between the S_1 and the T_1 state than between the higher S^* and T^* states, so that intersystem crossing occurred more rapidly between the higher energy singlet and triplet states. The triplet excitation then relaxed to the T_1 state via internal conversion in the triplet manifold. This mechanism also has been suggested to explain the higher population of the triplet state in solid films of P3HT upon pumping in the UV than obtained when pumping in the visible regime.[31] Our results show that for P3OT in solution, the energy difference between the higher excited singlet and triplet states does not result in a faster intersystem crossing than between the S_1 and T_1 states, indicating that the mechanism of intersystem crossing via higher lying singlet and triplet states is not competitive with that operating between the S^1 and T^1 states.

Turning our attention now to the fast decay component, we recall that the same functional form $e^{-(t/\tau)^{1/3}}$ was found for the long-lived PIA kinetics in films of P3OT.[7] A possible source of this decay form is one-dimensional diffusion in which the excitations diffuse along the polymer chains among randomly distributed recombination centers.[32,33] The relative magnitude [A in Eq. (6)] of the fast component for P3OT, P3HT, and T_{12} is 1.7, 0.9, and 0.3, respectively. As discussed earlier, the linear absorption data imply that P3OT has the shortest conjugation length of the three materials used in this study, and the highest density of defects. This may result in a higher fraction of the photoexcitations becoming charge-separated across conjugation breaks or defects in P3OT than in either P3HT or T_{12} (T_{12} should have the fewest charge-separated excitations due to its size). In films of P3OT, studies of the dichroic ratio have shown that the excitations giving rise to the stretched-exponential decay of the PIA are charge-separated excitations.[7] Therefore, we consider it possible that a small fraction of the photoexcitations seen in the early time regime in the thiophene solutions ($t<50$ ps) undergo charge-separation across conjugation breaks or defects and proceed to follow the same recombination pathway as in the film. The increase in the lifetime τ_2 from 1 ps for P3OT to 4 ps for T_{12} is to be expected from the one-dimensional diffusion model, since a higher density of defects leads to a shorter lifetime.[32]

CONCLUSION

Using transient photoinduced absorption we have observed the intersystem crossing from the S_1 state to the T_1 state in P3OT, P3HT, and T_{12} in solution. The intersystem crossing time is 1.2±0.1 ns, and is not affected by chain defects or impurities. By measuring the quantum efficiency of luminescence, we estimate the intrinsic radiative lifetime for singlet excitons in P3OT to be 2 ns, and the nonradiative lifetime to be 1.5 ns.

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